

SHOCKPROOF REFRACtORY CASTABLE ANODE ASSEMBLY

Field of the Invention

[0001] The present invention relates to methods for protecting electrode support structures from thermal shock, and degradation by the combination of HF/O₂ and other gases. More specifically, the present invention relates to protection of inert anode support structures from thermal shock during initial preheating and placement of the anode in an electrolytic cell and during operation when subjected to hot corrosive gases.

Background of the Invention

[0002] Aluminum is produced conventionally by the electrolysis of alumina dissolved in cryolite-based molten electrolytes at temperatures between about 850°C and 1000°C; the process is known as the Hall-Heroult process. This process is well known and described for example in U.S. Patent Specification No. 5,279,715 (La Camera et al.) A Hall-Heroult reduction cell typically comprises a steel shell having an insulating lining of refractory material, which in turn has a lining of carbon that contacts the molten constituents. Conductor bars connected to the negative pole of a direct current source are embedded in the carbon cathode substrate that forms the cell bottom floor. The carbon lining and cathode substrate have a useful life of three to eight years, or even less under adverse conditions. The deterioration of the cathode bottom is due to erosion and penetration of electrolyte and liquid aluminum as well as intercalation of sodium, which causes swelling and deformation of the cathode carbon blocks. In addition, the penetration of sodium species and other ingredients of cryolite or air leads to the

formation of toxic compounds including cyanides. Anodes are at least partially submerged in the bath and those anodes as well as their support structures are subject to the same conditions.

[0003] Electrolytic reduction cells must be heated from room temperature to approximately the desired 1000°C operating temperature before the production of metal can be initiated. Heating should be done gradually and evenly to avoid thermal shock to the cell components which can in turn cause breakage or spalling. The heating operation minimizes thermal shock to the lining, the electrodes and the support structure assemblies upon introduction of the electrolyte and molten metal to the cell. Prior art carbon anodes can be placed into the electrolyte at ambient temperature, and heated by the energy of the cell to operating temperatures, at which time the nominal current of the anode will be attained. Newer, ceramic inert anodes have much longer lives, but both the anodes and their supports are prone to thermal shock and therefore generally need to be preheated in a furnace or the like outside of the electrolytic cell prior to insertion into the hot electrolyte. The thermal shock/cracking can occur both during movement of the anodes into position and during their placement into the molten salt. Thermal shock relates to the thermal gradient (positive or negative) through the anode that occurs during the movement from the preheat furnace to the cell, and also upon insertion of the anodes into the molten salt. A thermal gradient as low as 50°C can cause cracking.

[0004] In the design of inert anodes for aluminum or other metals production, an array or assembly of anodes is mounted on a cast refractory support below a metal plate,

through which a continuous electrical path from the cell is provided. In this arrangement, it is necessary to provide protection of the metal plate and thermal insulation capacity for the entire assembly to meet heat balance requirements. A cast refractory support with adequate corrosion resistance to the molten bath and molten bath vapors can be used in 5 this application. The problem, however, is that most refractory materials are not able to withstand the severe thermal shock and gradients encountered during preheat operations without cracking or otherwise failing during service.

[0005] Use of steel fibrous fillers to provide superior thermal shock resistance over refractory castables having up to 1.2 vol.% fibers was recognized in a SIFCA (Slurry Infiltrated Fiber Castable) brochure "The Unique Refractory Solution," Wahl 10 Refractories, Inc., dated August 1, 1995, for furnace door jambs, metal stirring tools, skim blades and the like. Hackman, in US Patent Specification No. 5,308,572 taught a cementitious structural member which could be used as a refractory shape, having a reinforcing non-woven mat of 2 vol.% to 6 vol.% of cast stainless steel fibers. The 15 Ribbon Technology Corporation web site "Refractories" at http://www.ribtec.com/Products_refractories.htm, June 25, 2001 describes products made using rapidly solidified stainless steel fibers, from 1.58 cm (5/8") to 3.49 cm (1 3/8") long, in moldable refractories, to inhibit crack formation and resist corrosion. The fibers 20 used were ribbon shaped needles with a concave or "kidney" shaped cross-section and high specific surface area. The fibers were spun directly from a metal melt, with rapid cooling to freeze the metallurgical structure. A method of making similar fibers is taught

in U.S. Patent Specification No. 4,813,472 (Hackman et al.) This method also provides a non-circular surface free of surface lubricants usually present on circular "drawn" fibers. The Ribtec fibers can contain up to 36% nickel (maximum service temperature of 1,163°C) and 27% chromium (maximum service temperature of 1,099°C) as described at 5 the web site "Alloy Specifications" at <http://www.ribtec.com/alloys.htm>, May 23, 2000.

[0006] La Camera et al. U.S. 5,279,715 tried to protect cell components, including the newer ceramic inert anodes from thermal shock by electrowinning in a eutectic salt bath comprising NaF and AlF₃ operating in the range of 0.1 to 1.50 A/cm², at a low temperature of less than about 900°C and most preferably from 685°C to 850°C. In 10 another attempt to protect electrodes in an electrolysis cell from thermal shock during start-up, U.S. Patent Specification No. 4,265,717, (Wiltzius), taught protection of hollow cylindrical TiB₂ cathodes by inserting aluminum alloy plugs into the cathode cavity and further protecting the cathode with a heat dispersing metal jacket having an inside heat 15 insulating layer contacting the TiB₂. There, the heat insulating layer was made of expanded, fibrous kaolin-china clay (Al₂O₃ • 2SiO₂ • 2H₂O), which would subsequently dissolve in the molten electrolyte. Neither of the above solutions is completely successful.

[0007] Aluminum electrolysis cells have historically employed carbon anodes on a commercial scale. The energy and cost efficiency of aluminum smelting can be 20 significantly reduced with the use of inert, non-consumable, and dimensionally stable anodes. Use of inert anodes rather than traditional carbon anodes allows a highly

productive cell design to be utilized, thereby reducing capital costs. Significant environmental benefits are also realized because inert anodes produce essentially no CO₂ or CF₄ emissions.

[0008] Some examples of ceramic inert anode compositions are provided in U.S. Patent Specification Nos. 4,374,761; 4,399,008; 4,455,211; 4,582,585; 4,584,172; 4,620,905; 5,279,715; 5,794,112; 5,865,980; and 6,126,799 assigned to Alcoa Inc. These ceramic anodes are usually made by solid-state reaction of component oxides with repeated ball milling and then calcining to provide 100% ceramic structures comprising at least nickel and iron oxides with minor amounts of other oxides such as cobalt oxide. These anodes comprise a ceramic phase and may also comprise a metal phase. They are essentially void free and exhibit very low solubility, good dimensional stability and good corrosion resistance in Hall cell baths at 1000°C. The 4,374,761 patent for example mixed powdered dried Fe₂O₃ with NiO for 30 minutes, pressed the mixture at 25,000psi (17,225 kPa) to provide a bar, sintered the bar at 1125°C for 16 hours, crushed the bar, reground, finally repressed, and finally sintered at 1400°C, to provide a bar shaped electrode with a density of about 4.6 grams/cc. Ceramic inert anodes, unlike their carbon predecessors, can undergo thermal shock and cracking if heated or cooled too quickly. Better methods of protecting such ceramic inert anodes as well as the entire anode support assembly from thermal shock are needed.

Summary of the Invention

[0009] It is one of the main objects of this invention to protect inert cermet anode support assemblies from thermal shock and chemical reactants. It is another main object of the invention to provide a support assembly for an inert anode system in contact with a molten salt bath which is resistant to thermal shock and chemical reactants. These and other objects are accomplished by providing a support for an anode system in contact with a molten salt bath in an electrolysis apparatus, said support comprising a 50% to 95% dense (50% to 95% of theoretical density) castable refractory subject to attack by gases from the bath, where the refractory comprises refractory material and from 2 wt% to 20 wt.% of metal fibers, where the metal fibers are from 1 cm to 4 cm long, and have a length to thickness ratio of 500:1 to 20:1.

[0010] The invention also provides a support assembly for an inert anode system comprising at least one inert anode in contact with a molten salt bath in a metal electrolysis apparatus, where the inert anode is attached to a support system having a side subject to attack by gases from the bath, the support system consists essentially of a 50% to 95% dense castable refractory material having from 2 wt.% to 20 wt.% of metal fibers dispersed therethrough, where the fibers, are from 1 cm to 4 cm long, and where no more than 20 fibers per sq. cm. on average protrude through the outer side of the support system. The refractory material is preferably at least 55 wt.% alumina having a maximum service temperature of at least 1200°C, the fibers are preferably stainless steel with less than 22 wt. % nickel content, or nickel alloys or copper alloys, and optionally,

have a phosphate coating. If a substantial number of fibers protrude from the outer side of the refractory support, gases such as a combination of HF (from the bath) and O₂ (generated at the anode) will attack and corrode/dissolve the exposed fiber and then continue to react with other fibers at contact points within the refractory. By having 5 fibers present, if a crack were to start through the support wall the fibers would be able to stop the crack from propagating. The invention also includes an electrolytic reduction cell for the production of aluminum comprising the above described support assembly.

[0011] The invention also includes an electrolytic process for making a metal where an electrolyte reduction cell comprising at least one inert anode is attached to a 10 castable refractory support where the anodes and support contact a molten salt bath in an electrolysis apparatus at up to about 1050°C and where corrosive gases contact the inert anode and the support, and where metal is deposited from the molten salt bath, where said support comprises a 50% to 95% dense castable refractory subject to attack by gases from the bath, where the refractory comprises refractory material and from 2 wt.% to 20 15 wt.% of metal fibers, where the metal fibers are from 1 cm to 4 cm long and have a length to thickness ratio of 500:1 to 20:1.

[0012] These and other aspects of the present invention will be more apparent from the following description when considered in conjunction with the accompanying non-limiting drawings.

Brief Description of the Drawings

[0013] Figure 1, which best shows the invention, is a cross-sectional view of an inert anode system with a plurality of anodes in contact with a molten salt bath, used for example in aluminum processing, where the anodes are attached to a support system of 5 dense refractory having metal fibers therethrough;

[0014] Figure 2 is a cross-section view of the wall of the refractory support system showing the metal fibers;

[0015] Figure 3 is a three dimensional magnified view of a preferred, non-circular, ribbon shaped fiber having a "kidney" shaped cross-section;

[0016] Figure 4 is a front view of part of the refractory support with an idealized magnified 1 sq. cm. section showing protruding fibers; and

[0017] Figure 5 is a graph of stress vs. strain for a refractory material containing 0 wt.%, 3 wt.% and 6 wt.% long uncoated metal fibers.

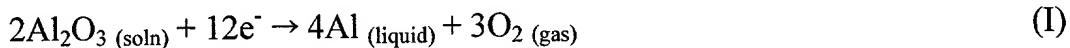
Detailed Description of Preferred Embodiments

[0018] Referring now to Fig. 1, an electrolytic cell comprising inert anode system 10 is shown in an electrolysis apparatus, used for example to produce aluminum, and comprises a support system and a plurality of inert anodes 14 and 14'. The support system includes a refractory support 12 to which the inert anodes are in contact and attached. The refractory support material can be a flat plate structure, or, for example, the 20 hollow box type structure shown. Metal bolts 16 anchor the inert anodes to the refractory support 12 and to a top metal, usually steel plate 18 anchored to the refractory support 12

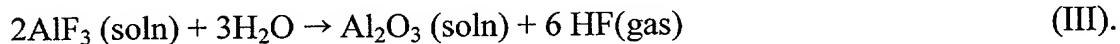
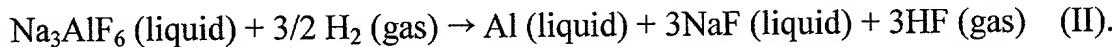
by metal anchors 20 or the like. The entire inert anode system is attached to a massive metal support 22. The inert anode system can be quite large, with the length 30 of the refractory support being from about 2.44 m to 3.66 (8 feet to 12 feet), and the wall thickness 31 being from about 5cm to 20 cm. The refractory support 12 has an outer or 5 exterior side 24 and as shown, an interior side 26. The interior of the refractory support 12 can be filled with layers of low density ceramic boards 28 as shown, or insulating mat made from ceramic fibers, or other materials, or left hollow.

[0019] Gases 32 from the molten salt bath 34 and anode 14, 14' can be very aggressive even to stainless steel, especially several gases in combination. The gases shown as circles (bubbles) 32 from either the bath or the anodes 14' (only gas from the 10 two outer anodes are shown for sake of simplicity) pass above the bath 34 as the gas flow arrows 36. The molten salt bath 34 usually used in the Hall process to produce aluminum is based on molten cryolite (as NaF plus AlF₃), at a bath weight ratio of NaF to AlF₃ in a range of about 1.0:1 to 1.4:1 and at a temperature usually from about 850°C to 1050°C, 15 preferably from 950°C to 975°C. Attempts have been made to run the bath temperature of the cell at lower temperatures, as in La Camera et al. U.S. 5,279,715, which also discusses other useful salt baths and is herein incorporated by reference. Additionally, a variety of bath additives can be added for various purposes. The inert anodes are not totally immersed in the molten bath, usually the top edge of the anode is above the bath a 20 distance 38, usually from about 7.5cm to 19 cm, called the gas or vapor space. The gases 32 most commonly generated include HF, O₂, NaAlF_x, Na₂SiF₅, NaF, and Na₂Al₂F₈. A

combination of HF and O₂ is particularly corrosive to metals especially at temperatures over about 400°C. Oxygen is generated at the anodes according to the reaction:



and HF is generated from the bath according to the reactions (II) and (III):



[0020] The source of water is the chemically bound water intrinsic to the smelting grade alumina fed to the smelting cell. The temperature of the refractory castable support 12 at points 13 where there might be HF and O₂ contact is about 700°C to 1000°C depending on the distance from the molten cryolite.

[0021] Fig. 2 shows the refractory support 12 of this invention having external, exposed exterior side 24 and interior side 26, with long, thin, metal fibers 40 contained within the refractory support 12. Metal fibers are very much preferred, since most ceramic fibers over time at operating temperatures over 800°C would become part of the refractory material. Some fibers have cross over points 42 but, preferably, have a substantially random dispersal arrangement as at points 44, 46, 50 and 52. A highly mechanically locked or fiber cluster configuration is not desirable even though there is a random dispersal. Some fibers 40 pass through the exterior side wall 24 as at points 46 and are subject to chemical corrosive attack by a variety of gases from the bath and anode which can start degradation at point 46 and continue through the refractory matrix 48 to various cross over points 50 and continue corrosive effects to, for example, point 52 deep

in the refractory matrix. On the very rare occasion that thermal shock might start a crack 56, and cause the crack to propagate as shown at 58, use of fibers 60 will help stop the effect and maintain the integrity of the support, as shown at the top of Fig. 2.

[0022] Also shown in the refractory matrix 48 are filler particles 54 usually of a 5 ceramic material present in amounts of 1 wt.% to 45 wt.% of the total weight of refractory material plus fibers, preferably from about 10 wt.% to about 30 wt.%. The term "ceramic filler" is used here to describe a material stable at elevated temperatures. This ceramic filler is a ceramic based material, and is used to increase toughness, reduce cost and control thermal conductivity and can be selected, for example from the group 10 consisting of shale, stone aggregate, their mixtures and the like, most preferably having a particle size range of from about 0.5 mm to about 20 mm, and does not include materials such as nickel ferrite. The metal fibers 40 are present from 2 wt.% to 20 wt.%, based on total refractory matrix plus filler weight, preferably 3 wt% to 10 wt%, of the total weight 15 of refractory materials plus any filler. A generally useful support can contain for example 3 wt% to 7 wt.% fibers, 10 wt.% filler, with the remainder being refractory matrix. The refractory material forming the matrix 48 of refractory support 12 can comprise a wide variety of materials. The refractory material is preferably mostly alumina (Al_2O_3), preferably as a castable refractory, that is, those refractories that are supplied as dry mixed materials that need to be combined with water or other specified 20 liquid and are mixed together at the application site. The material is applied by pouring it into a mold with specific features and dimensions, for example, holes where the bolts 16

pass through, as shown in Fig. 1, eliminating most drilling and other machining; all saving costs. After pouring, vibration of the filled mold can be used for removing trapped gases and for making the material flow and find its own level. Conventional castables are usually poured whereas low and ultralow cement castables are poured 5 followed vibration.

[0023] While conventional castable refractories were considered low strength over 400°C, most new materials have maximum operating temperatures much higher, for example: Permotech Alpha, containing no fibers, and having a chemical analysis of 95% 10 Al_2O_3 and 4.0% lime (CaO) as main ingredients has a maximum service temperature of 1427°C; Permotech Beta 2HPSL, self-leveling castable refractory, with no fibers or with about 3 wt.% Number 304 stainless steel fibers, and having a chemical analysis of about containing 65.8% Al_2O_3 , 26.2% SiO_2 , and 1.4% lime (CaO) as main ingredients has a maximum service temperature of about 1427°C; Permotech Beta 2SL, castable refractory containing stainless steel fibers and having a chemical analysis of 60.8% Al_2O_3 , 31.0% 15 SiO_2 , and 1.4% lime (CaO) as main ingredients has a maximum service (oxidation) temperature of 1204°C; and Permotech Beta-X677SL castable refractory containing stainless steel fibers and having a chemical analysis of 57.9% Al_2O_3 , 39.0 SiO_2 and 1.4% lime (CaO) as main ingredients has a maximum service (oxidation) temperature of 20 1204°C. All of these castable refractories are sold commercially by Permotech, Inc., as described in "Castables for the Aluminum Industry" at the website www.permotech.net.

[0024] In the material system Al_2O_3 - SiO_2 - CaO , during curing calcium aluminates are formed, as well as silicates. The calcium aluminate $(\text{CaO})\bullet(\text{Al}_2\text{O}_3)$ is the most important aluminate in high aluminum cements since it provides a cement type behavior, bonding the aggregate together. Impurities can include MgO , Na_2O and Fe_2O_3 which 5 may be present up to about 8% total. The $\text{Al}_2\text{O}_3\bullet\text{SiO}_2\bullet\text{CaO}$ support should have a maximum service temperature of at least 1200°C.

[0025] The fibers are most preferably metal, since ceramic fibers can over time become homogeneous with the refractory matrix and add no strength or support. The fibers can be from 1 cm to 4 cm long, preferably from 1 cm to 2 cm long since the wall of 10 the castable refractory support is usually about 5 cm to 7 cm thick. Over 4 cm long, fibers can more easily have primarily a crossing relationship with each other in the matrix and can more easily protrude from the wall of the refractory support, as at 46 in Fig. 2, and be susceptible to corrosion. Most preferred fibers are at least one of stainless steel, or nickel alloy or copper alloy, and have a length to thickness ratio – aspect ratio - of 500:1 15 to 20:1, most preferably 100:1 to 50:1. Over a 500:1 ratio the fibers are hard to disperse evenly, have many cross over points, and are weak or of low strength. Under a 20:1 ratio the fibers provide little reinforcement benefit and add significant weight and cost. Nickel alloys most useful will contain at least 25 wt.% preferably at least 50 wt.% Ni along with 20 elements such as Cr, Fe, Co, Al, C, Mn and Si among others such as alloys sold under the trademarks Monel, Inconel and Hastelloy. Useful copper alloys will contain at least 50

wt.% Cu along with elements such as Fe, Sn, Zn, Al, Pb, S and C among others. Even if the copper alloy should soften or melt, it will still provide good thermal shock resistance.

[0026] The fibers can have an optional phosphate coating from about 0.5 nanometers to about 5 nanometers thick. We have found that the phosphate cleans any 5 oxides and contaminants off the fiber so it is tightly gripped within the castable refractory matrix. The phosphate also acts as a coupling and bonding agent, promoting good bonding to the refractory matrix, which is important in preventing any cracks or crack propagation, as at points 56 and 58 in Fig. 2. Under an average 0.5 nanometer thick phosphate coating, the coating is discontinuous over the surface of the fiber.

10 Discontinuous phosphate coatings reduce the interfacial bond strength between the fiber and the ceramic matrix. Over a 5 nanometers thick phosphate coating, no additional benefit is gained and can contribute to poor interfacial bond strength since the ceramic material can react with the phosphate and not the surface of the fiber.

[0027] The coating preferably comprises an oxide of phosphorus, for example 15 phosphorus compounds containing (PO_4) moieties and can be applied as phosphonic acid, phosphinic acid, phosphoric acid, meta phosphoric acid, phosphorus pentoxide and phosphorus trioxide. Metal salts are not preferred since they are less reactive to the surface of the stainless steel fiber and the ceramic matrix. The phosphorus containing coating can be applied by dipping or spraying the phosphorus containing solution

20 **[0028]** The most preferred fiber 40 shape and composition, is the high aspect, non-circular, not drawn, ribbon-shaped needle fiber generally shown in Fig. 3 and having a

concave or kidney cross-section or shape. The nickel content for stainless steel fibers can be up to about 22 wt.% of the stainless steel composition (that is from 0 wt.% to 22 wt.%). Chromium content for stainless steel fibers should be below 50 wt.%, otherwise the fibers become too brittle and have low fracture toughness. One useful stainless steel 5 fiber, for example, is Stainless 446, which contains about 23-27 wt.% Cr, no Ni and minor amounts of Mn and Si.

[0029] Additionally, the coefficient of thermal expansion (CTE) of the fibers should be low, that is, up to about 16×10^{-6} at 871°C. The maximum continuous service 10 temperature, or critical oxidation temperature, of the fibers should be at least 800°C (1470°F). A useful fiber is sold by Ribtec as ME4446, with 0% Ni and about 25% Cr with a continuous service temperature of 1099°C (2010°F) and a CTE of 13.1×10^{-6} at 871°C. They are available in 1.9 cm x 0.038 cm (3/4 in x 0.015in) and 1.58 cm x 0.20 cm (5/8 in. x 0.008 in.) sizes.

[0030] Fig. 4 shows a 1 sq. cm. idealized, magnified view of the exposed side 24 of the castable refractory support 12, showing fiber protrusion at for example point 46. 15 As shown in Fig. 4, seven fibers are shown protruding through the exposed side for possible contact with harmful gases in an aluminum smelting environment. Up to 20 fiber protrusions per sq. cm., on average are acceptable, by that is meant that 50% of the area exposed side 24 of the refractory support 12 can have up to 20 fiber protrusions per 20 sq. cm., where a few 1 sq. cm areas over this value on the entire exposed side would not

be considered harmful. Preferably there are only up to 10 fiber protrusions per sq. cm., on average, most preferably there are no fiber protrusions at all.

[0031] By way of further illustration of the invention the following non-limiting examples are set forth below.

5

EXAMPLE

[0032] Stainless steel fibers having sizes of 1.9 cm x 0.038 cm (3/4 in. x 0.015 in), providing a length to thickness ratio of 50:1, with 0% Ni and from 23% to 27% Cr, sold commercially as Ribtec-GR 304 stainless steel fibers were used in this example. The fibers had a critical oxidation temperature of 1038°C (1900°F) and a Coefficient of Thermal Expansion of 11.2×10^{-6} at 871°C. These fibers do not have a circular cross-section but have a high surface area kidney shaped cross section, as shown in Fig. 3. The fibers did not have the optional phosphate coating.

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[0033] Portions of the fibers were mixed with a castable refractory powder having a chemical analysis of 71.0% of Al₂O₃, 24.0 % of SiO₂, 1.5 % CaO and 3.5% other materials, sold commercially by Permatech Inc. as Permatech Beta 70 HP. Ten samples were made as set out in Table 1 below:

15

20

<u>Sample Nos.</u>	<u>Stainless Fiber</u>
1-4	0 wt.%
5-7	3 wt.%
8-10	6 wt.%

100%
Ductile
Bridgeman
10

[0034] Samples 5-10 were dry mixed and then mixed with water to provide a slurry. The slurry was then pound into molds and allowed to dry followed by heating. Finally, stress strength in psi vs. strain % (toughness) tests were run to determine the modulus of elasticity ("MOE") at various % strain points. The MOE is a measure of 5 strength, where the greater the strength retained at increasing stress shows good toughness. This test followed a modified ASTM C 133-97 method "Standard Test Methods for Cold Crushing Strength and Modulus of Rupture of Refractories" to measure the MOR (modulus of rupture) values. The modifications were that the test bars were 2.54 cm x 2.54 cm x 17.8 cm instead of 5 cm x 5 cm x 22.8 cm, the bearing cylinders were 12.7 cm apart instead of 17.8 cm, and three instead of five specimens were analyzed. The MOR values were calculated using the following equation.

MOR = $3PL/2b(d \exp 2)$, where MOR = the modulus of rupture, P = maximum applied at rupture, L = span between supports, b = width of specimen, and d = depth of specimen, where d has an exponent of 2.

[0035] The results are provided in Fig. 5, showing that samples with 0 wt% fibers completely lost strength after about a 0.5% strain increase. The stress values were:

[0036] Samples 1-4 (0 wt% fibers) = 4242 +303 psi

[0037] Samples 5-7 (3 wt% fibers) = 3099 + 115 psi

[0038] Samples 8-10 (6 wt% fibers) = 2240 + 8 psi

[0039] The samples with 3 wt.% fibers showed dramatic improvement in reaction 20 to increasing strain while still maintaining good (high) initial stress values. The samples

with 6 wt.% fibers showed superiority at high % strain values. Use of a phosphorus containing coating on the fibers are expected to provide even more improved results.

[0040] All the sides of Samples 5-10 were closely observed and few protruding fibers were seen perhaps 5 to 10 per sq. cm. Upon breaking some of the Samples 5-10, 5 the fibers were seen to have a random orientation. Upon cracking some of the samples, it was observed that the fibers made it very difficult to propagate the crack.